Investigation of the origin and distribution of heavy metals around Ebenezer Dam, Limpopo Province, South Africa

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Abstract

This study was based on the outcome of the soil geochemical survey which was conducted by the Council for Geoscience around Ebenezer Dam during 1995-1996, the results of which indicated high concentrations of lead (Pb), zinc (Zn) and arsenic (As). The current study therefore focused on the origin and distribution patterns of Pb, Zn, Cu, As and Cr within the environs of Ebenezer Dam and their potential impacts on the environment and human health. The work involved soil, sediment, rock and water sampling and analysis. Atomic absorption and x-ray fluorescence spectrometry were used to determine the metal concentrations. The occurrence of anomalous concentrations of these metals in the study area was established. The anomalies registered maximum concentrations of (mg/g): 57 for Pb, 157 for Zn, 313 for Cu, 73 for As and 888 for Cr. The concentrations of these metals in sediments along the streams were high near the anomalies, but decreased downstream. Concentrations of heavy metals in water around the Ebenezer Dam were found to be less than 0.01 mg/g , except for As which was less than 1.0 mg/g. Thus Pb, Zn, Cu and Cr values were below the target water quality ranges for domestic, irrigation, livestock watering and aquatic ecosystem use. The study confirmed that the distribution of heavy metals in this area is localised within and around the source rocks that are felsic in nature, namely; granites and pegmatites that formed domes in the area.

Keywords: Ebenezer Dam, heavy metals, distribution patterns, anomalies

Introduction

Concern over the effects of heavy metals on the environment and human health is increasing with rapid economic development and population growth. Exploitation of mineral resources, agricultural activities and urbanisation result in disturbance of the natural environment and water pollution. This, in conjunction with natural geological processes, leads to the release of elements/metals into the environment. Most of these heavy metals are re-deposited and concentrated in soils, surface water and groundwater (Plant et al., 1996).

Geochemistry, particularly, the surface distribution and concentration of trace elements, can be difficult to predict from geological maps (Simpson et al., 1991). Thus, in many developed countries, such as Britain, Canada, Scandinavia and Australia, geochemical mapping has been incorporated into the strategic systematic geoscience survey, which uses geochemical data to prepare modern geochemical maps in line with the International Geochemical Baseline. In developing countries there is an urgent need for high resolution geochemical data which are adequate for environmental and epidemiological studies (WHO, 1998).

The Council for Geoscience of South Africa has already embarked on such projects in a number of provinces and this project was a follow-up to this work, being based on the outcome of research conducted in the area around Ebenezer Dam. The area was sampled during 1995-1996 and the soil analysis from this area indicated high concentrations of lead (Pb), zinc (Zn) and arsenic (As) (Szczesniak et al., 2001). The recommendation from this initial work was that a detailed investigation needed to be done in order to establish the nature and source of geochemical anomalies and their impacts on the environment.

The Ebenezer area, which covers Haenertsburg town and the Ebenezer Dam, is found about 60 km to the east of Polokwane city and lies between 23°48’00’’ and 24°00’00’’ latitude and 29°52’00’’ and 30°06’00’ longitude (Fig. 1). The area is densely forested, mountainous and has fenced farms and plantations. The dam covers about 66 km^2. The dam water is mainly used for domestic, agricultural, livestock and recreational purposes.

Materials and analytical techniques

Soil sampling: Initial sampling covered the entire study area at an interval of 500 m along defined grids. About 2 kg of soil samples were collected (50 samples) at a depth of 10-15 cm. This was later followed by detailed soil sampling of targets at 100 m intervals along profiles, 200 m apart, and a total of 52 samples was collected.

Sediment sampling: This involved sampling along streams that cut through or run close to the anomalous targets, including those that feed Ebenezer Dam (Fig. 2). A total of 30 sediment samples were collected along the streams at an interval of 200 m, each sample weighing about 2 kg.

Water sampling: Water samples were collected along the shoreline of the dam and upstream at an interval of 200 m from the shoreline (Fig. 2). Ten samples were collected in 250 mℓ bottles. Before sampling, the water bottle was rinsed with water to be sampled, and the pH and electrical conductivity readings

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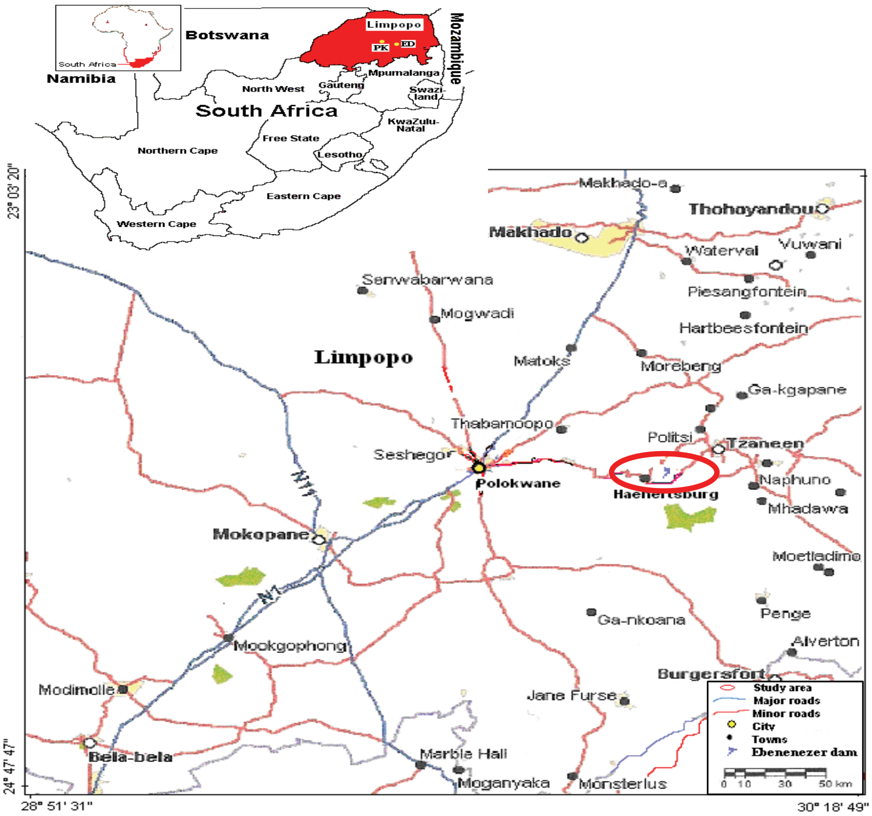

Figure 1
Location map of the Ebenezer Dam and its environs (Source: Google maps)

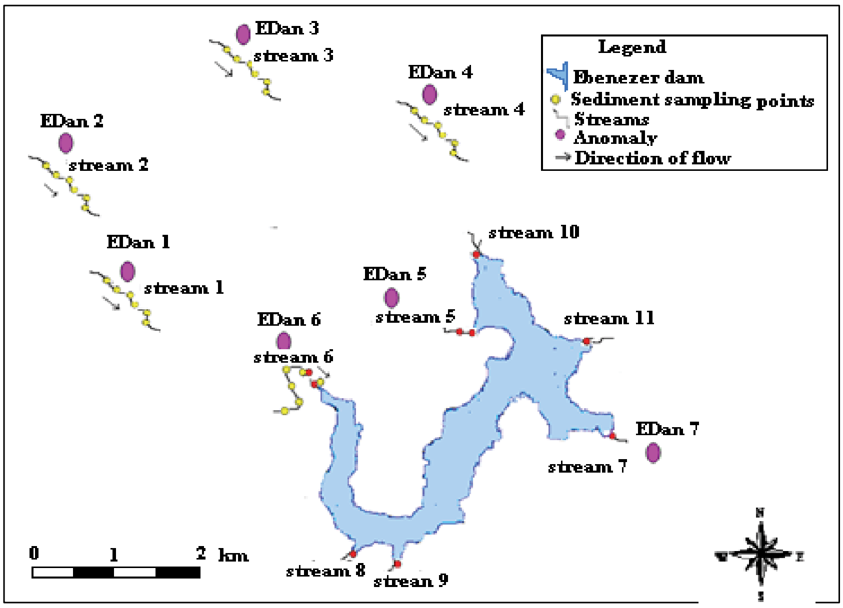

Figure 2
A sketch map of sediment and water sampling points in Ebenezer area

were taken, using a WTW Multi 340i meter. The pH meter was first calibrated using standard buffers of pH 7 and pH 4. Electrical conductivity (EC) measurements were obtained by immersing a conductivity electrode into each water sample and leaving the electrode to stabilise for about 2 min. The electrodes were rinsed with distilled water after each sample.

Rock sampling: The concentrations of heavy metals in the soil were used to plot the anomaly map for Pb, Zn, Cu, As and Cr. These resulted in the identification of 5 targets from which 5 rock specimens were collected for further analysis.

Sample preparation and analysis: Soil and sediment samples were dried and milled into powder form. The samples were then digested, using aquaregia (1 part HNO_3 + 3 parts HCl by volume) and analysed, using atomic absorption spectrometry (AAS). Water samples were also analysed for Pb, Zn, Cu, As and Cr, using the same instrument; de-ionised water was used as a blank. Rock samples were crushed and milled into powder form then analysed, at the Council for Geoscience in Pretoria, using x-ray fluorescence spectrometry. The international dolerite reference materials (SARM 50) were used. The results of these analyses are presented in Tables 1, 2, 3 and 4.

Table 1
Results of concentrations of heavy metals in soils, sediments and rocks (mg/g)

Heavy metals	Anomaly 1								Anomaly 2								
	Rock	Soil	Sediments (Stream 1)					mean	Rock	Soil	Sediments (Stream 2)						mean
Pb	34	10	7	12	14	12	8	5	10	1	10	9	11	5	8	11	5	8

Heavy metals	Rock	Soil	Sediments						mean	Rock	Soil	Sediments						mean
Anomaly 1 / Anomaly 2			(Stream 1)									(Stream 2)						
Pb	34	10	7	12	14	12	8	5	10	1	10	9	11	5	8	11	5	8
Zn	12	30	41	30	41	49	22	25	35	2	22	15	30	20	34	40	17	26
Cu	4.6	43	62	38	66	74	47	54	57	3.9	32	12	18	12	18	30	14	17
As	3	4	18	30	26	34	20	6	22	3	4	20	10	18	14	8	12	14
Cr	21	77	71	119	137	96	92	50	94	6.8	54	29	89	26	38	43	25	42
Anomaly 3 / Anomaly 4	Rock	Soil	Sediments (Stream 3)						mean	Rock	Soil	Sediments (Stream 4)						mean
Pb	32	11	8	5	5	4	7	5	8	1	9	9	10	9	9	5	7	8
Zn	4.8	17	27	15	24	33	24	15	28	105	25	41	32	30	44	22	27	33
Cu	3.6	38	26	14	18	16	20	23	32	192	50	65	41	4	40	20	36	40
As	3	4	14	18	18	18	12	14	17	3	4	10	8	4	8	18	8	9
Cr	16.3	167	106	110	88	41	55	85	72	67	192	208	203	324	250	119	211	219
Anomaly 6	Rock	Soil	Sediments (Stream 6)						mean									
Pb	13	8	18	3	4	6	5	7	7									
Zn	34	60	54	17	38	44	31	38	37									
Cu	8.8	98	54	12	46	53	34	32	39									
As	3	4	42	22	12	12	18	14	20									
Cr	15	135	121	181	72	107	187	83	125									

Table 2
Heavy metal concentrations, pH and electrical conductivity measurements of water from Ebenezer Dam

	Heavy metal concentrations (mg/g) at 26 °C									Target water quality range for water use in mg/g (DWAF, 1996)			
	Stream 5	Stream 6	Stream 7	Stream 8	Stream 9	Stream 10	Stream 11	Blank	Average	Domestic	Irrigation	Livestock watering	Aquatic ecosystem
Pb	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01		0.01	0.2	0.1	0.01
Zn	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01		3	1	20	2
Cu	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01		1	2	10	1.4
As	<1	<1	<1	<1	<1	<1	<1	<1		0.01	0.1	1	0.05
Cr	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01		0.05	0.1	1	20
pH	7.5	7.4	7.4	7.5	7.3	7.4	7.6	-	7.4	6.5-8.4			
EC mS/m	68	94	54	69	70	50	46	-	64.5	0 -70 mS/m			

Table 3
Major oxides (wt %) of rock samples collected in the Ebenezer area

Major Oxides	Sample ID					SARM 50		Standard deviation
	Feldspathic Pegmatite (EDr 1)	Quartzite (EDr 2)	Pegmatite (EDr 3)	Leuco-granite (EDr 4)	Granite (EDr 6)	Results	Certified	
SiO_2	73.22	98.90	76.99	68.84	71.24	51.22	51.56	0.2404
TiO_2	0.08	0.02	0.05	0.17	0.28	0.83	0.86	0.0212
Al_2O_3	14.97	0.41	14.65	17.26	15.97	15.19	15.28	0.0636
Fe_2O_3(t)	1.03	0.73	0.87	0.53	2.41	11.05	11.0	0.0354
MnO	0.015	0.011	0.015	0.043	0.030	0.175	0.170	0.0035
MgO	0.16	0.06	0.07	0.06	0.72	7.51	7.57	0.0424
CaO	0.37	0.02	0.33	0.52	2.49	10.82	10.8	0.0141
Na_2O	2.94	0.08	2.99	5.05	5.04	2.13	2.30	0.1202
K_2O	6.82	0.03	5.26	6.16	1.39	0.65	0.61	0.0283
P_2O_5	0.023	0.006	0.020	0.017	0.095	0.163	0.150	0.0092
Cr_2O_3	0.003	0.004	0.004	<0.001	0.005	0.047	0.052	0.0035
L.O.I.	0.26	0.11	0.35	1.10	0.84	-0.15	-0.89	0.5233
Total	99.89	100.17	101.61	99.75	100.50	99.63	99.46	0.1202
H_2O^-	0.22	0.13	0.35	0.53	0.28	0.18		0.0212

SARM-50 is an international dolerite reference material from MINTEK

Table 4
Trace element concentrations (mg/g) of rocks collected in the Ebenezer area with mean trace element abundance of major rock types (mg/g), (Krauskopf, 1967; Rose et al., 1979; Alloway et al., 1997)

Heavy metals	Granitic igneous rocks	Mafic igneous rocks	Results of specimen collected				
			Feldspathic Pegmatite EDr 1	Quartzite (EDr 2)	Pegmatite (EDr 3)	Leuco-granite (EDr 4)	Granite (EDr 6)
As	1.5	1.5	<4	<4	<4	<4	<4
Co	1	35	2.3	1.7	2.2	1.3	5.7
Cr	4	200	5.7	6.8	<3	6.9	15
Cu	13	90	4.6	3.9	3.6	2.6	8.8
Mo	2	1	<2	<2	<2	<2	<2
Pb	24	3	34	<2	32	24	13
Se	0.05	0.05	<1	<1	<1	<1	<1
TI	1.1	0.08	<3	<3	<3	<3	<3
U	4.4	0.43	<2	<2	2.3	<2	<2
W	1.5	0.36	<3	<3	<3	<3	<3
Zn	52	100	12	<3	4.8	8.2	34

GSS-1 is a soil reference material from IGGE, China

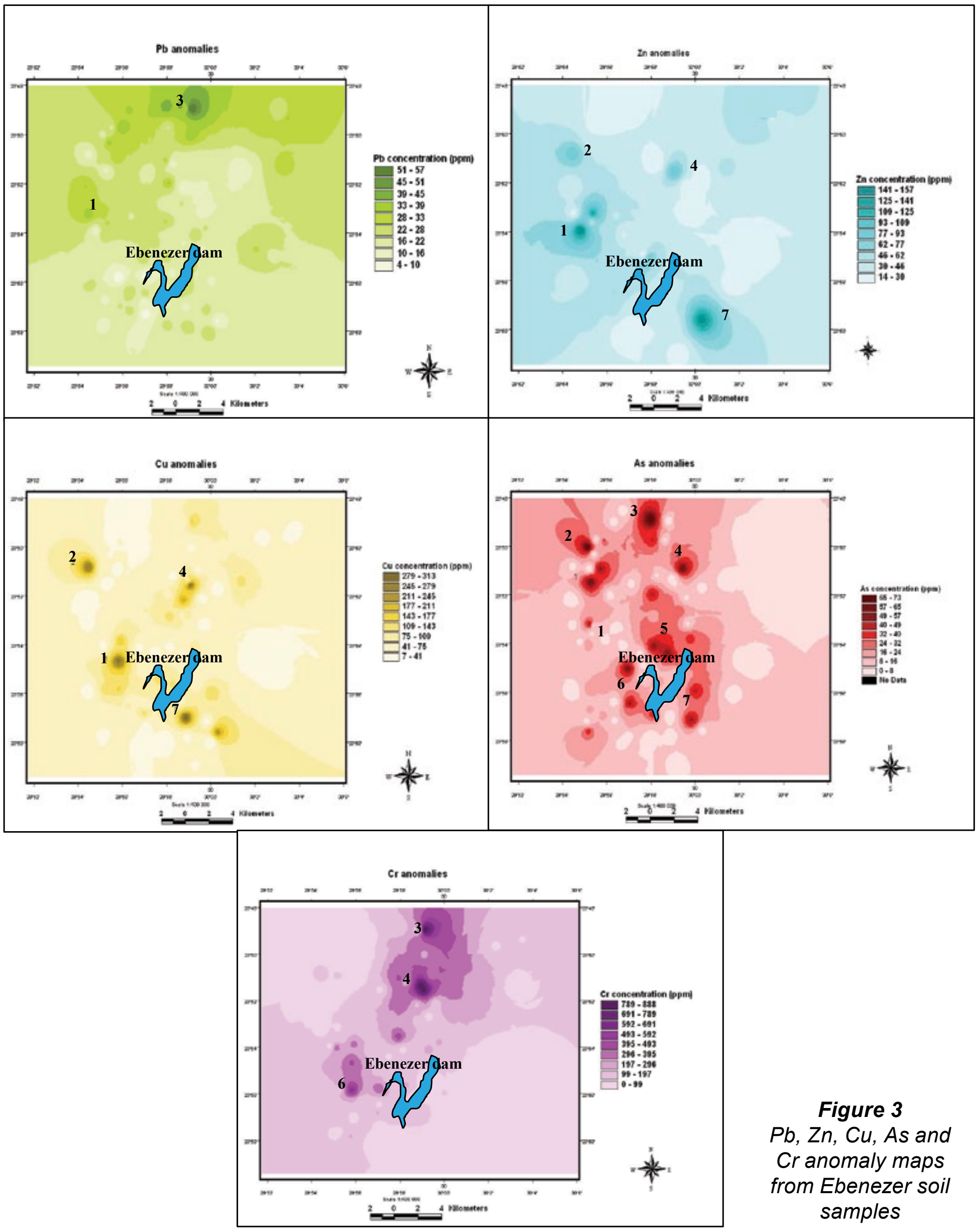

Figure 3
Pb, Zn, Cu, As and Cr anomaly maps from Ebenezer soil samples

Results and discussion

Concentrations of heavy metals in soils, sediments and rocks

Concentrations of Pb, Zn, Cu, As and Cr in soils were used to plot the anomalous map using ArcView 3.2 software (Fig. 3), from which the location map of these anomalies with reference to the dam was deduced (Fig. 4). The concentrations of Zn, Cu, As and Cr were found to be higher in soils and sediments but lower in rocks, with the exception of rock sample EDr 4 at Anomaly 4 (Fig. 5).

A comparison of the distribution pattern of heavy metals along the profiles over the anomalies showed a general increase in concentration from the base, along the slope, to the top part of the domes. For example, Zn distribution along the profiles over Anomaly 1 showed an increase in concentration from the base (25 mg/g), along the slope (30 mg/g) and at the top (39 mg/g) of the anomaly (Table 5 and Fig. 6). However, along Profile P3 there was a lower Zn value on the Southern slope of the anomaly. The stream registered higher concentrations near the anomaly and a decrease downstream. For example, Zn in Stream 1 had a concentration of 41 mg/g near the anomaly, but this decreased to 25 mg/g downstream (Table 1).

Table 5
Zn concentrations in soils along profiles at Anomaly 1

	P1	P2	P3	Average
Base$_1$ (B$_1$)	22	29	23	25
Slope$_1$ (S$_1$)	29	33	19	27
Top part (T)	46	37	34	39
Slope$_2$ (S$_2$)	37	31	31	33
Base$_2$ (B$_2$)	29	24	25	26

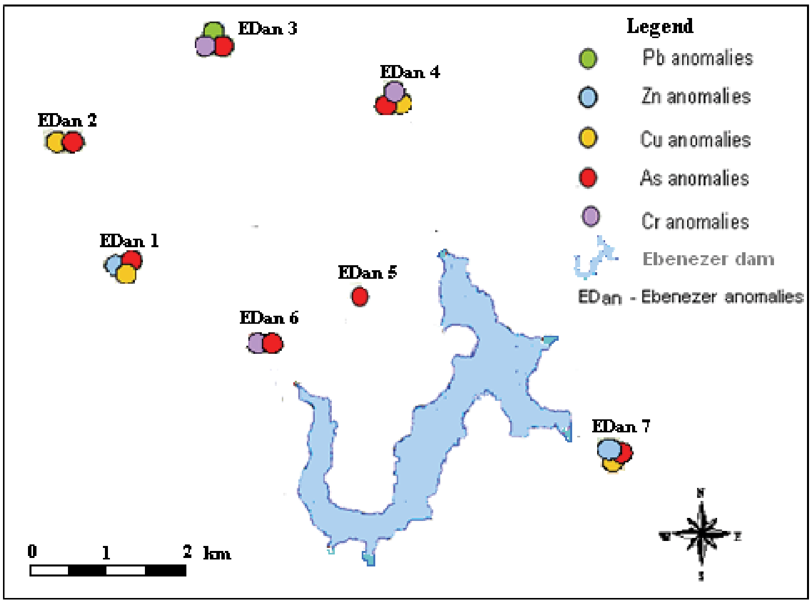

Figure 4
Location map of heavy metal anomalies

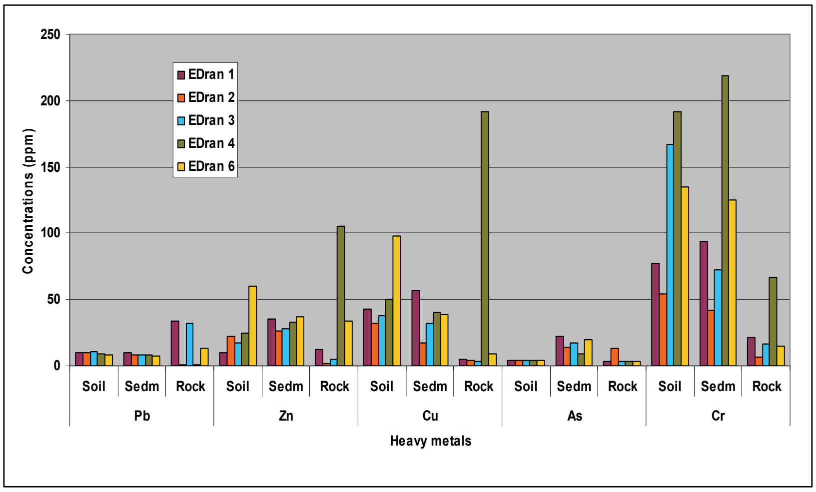

Figure 5
Concentrations of heavy metals in soils, sediments and rocks

Heavy metal concentrations in water

The concentration values of Pb, Zn, Cu and Cr in water were found to be below the detection limit (0.01 mg/g) of the AAS. This was also the case with As (< 1.0 mg/g). The concentrations of Pb, Zn, Cu, As and Cr were compared with the maximum allowable limit for domestic, agricultural, livestock and aquatic eco-system water quality and Pb, Zn, Cu and Cr were found to be below the maximum acceptable limit values. At the current level of analysis, the concentration of As in water was less than 1.0 mg/g and was found to be below the maximum acceptable limit value for livestock use (Table 2).

pH and electrical conductivity levels in water

The highest pH of 7.60 was obtained at the shoreline of Stream 11 on the north-eastern part of Ebenezer Dam and the lowest pH of 7.29 was obtained at Stream 9 on the southern part of the dam (Fig. 2). However, the overall assessment of the water pH indicated an average pH of 7.4 (Table 2). The pH of Ebenezer Dam falls within the target water quality range (6.5-8.4) set by DWAF (1996) for domestic, agricultural, livestock and aquatic ecosystem uses (Fig. 7).

The electrical conductivity water quality limit for domestic use is 70 mS/m (DWAF, 1996). The electrical conductivity for streams flowing into Ebenezer Dam was found to be within the limit for domestic water use (46-70 mS/m), with the exception of Stream 6, with a conductivity of 94 mS/m (Table 2).

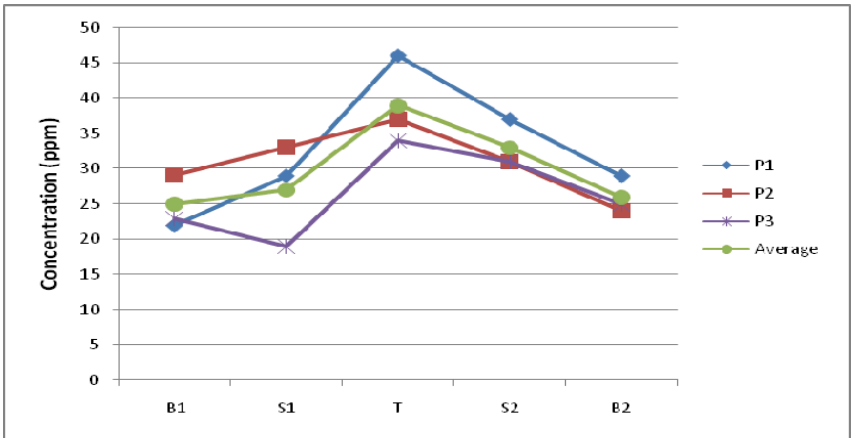

Figure 6
Concentration of Zn along the profiles over Anomaly 1

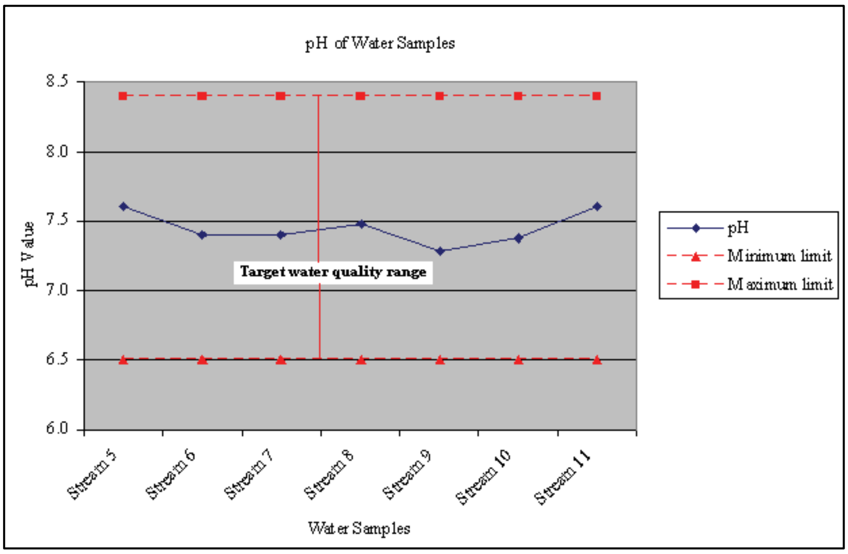

Figure 7
A comparison of the water pH with the permissible target water quality range

Analysis of major oxides and trace elements

The geochemical variations of country rocks can be obtained by using X-Y scatter graphs, plotting concentrations of major oxides (Rigby et al., 2008). Consequently, X-Y Scatter graphs were used to plot the concentrations of major oxides, Al_2O_3 vs. Fe_2O_3 + MgO% and SiO_2 vs. Fe_2O_3 + MgO%, in order to classify and confirm the rock types (Fig. 8).

Acidic or felsic igneous rocks are defined as rocks with high silica content, greater than 65% SiO_2, but with low ferro-magnesium values. For example, granites and pegmatites have an average SiO_2% and Al_2O_3% of 72% and 14%, respectively (Philpotts et al., 2009). Consequently, the rocks responsible for heavy metal anomalies in this area were found to be felsic, with high silica values and low ferro-magnesian content (Fig. 8). For example, Specimen EDr 2 registered 98.9% SiO_2 (Table 3), which meant that it consists almost entirely of silica (quartz). This rock was confirmed to be quartzite.

Trace element analysis of rock samples revealed high values for some metals within the rock. For example, the concentration of Pb in pegmatite was between 32-34 mg/g compared to the background value of 24 mg/g (Table 4). A similar trend was observed in the case of Cr, which was 6.9 mg/g and 15 mg/g in granite, against a background value of 4 mg/g. From this it can be deduced that the heavy metals originated from these rocks and that their elevated values were due to weathering and residual accumulation. This is further confirmed by their values within the dome-shaped structure, with highest values at the top (Fig. 6).

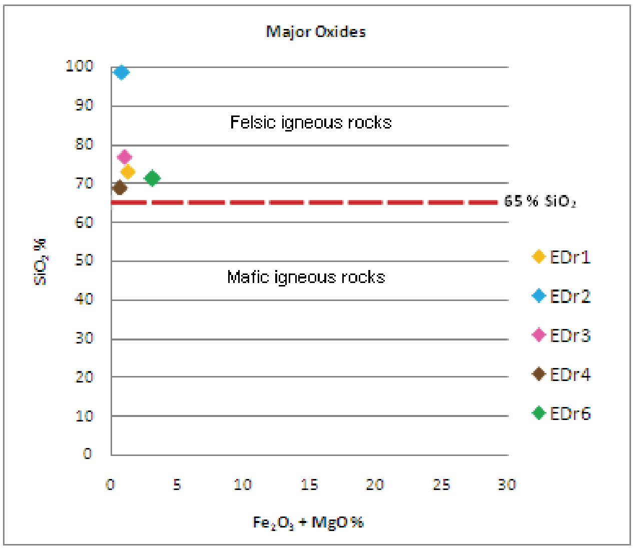

Figure 8
Plot of major oxides in rock specimens from Ebenezer: SiO_2 vs. Fe_2O_3 + MgO%

Conclusion

Based on the analysis of field and analytical data obtained from this study, it was concluded that the heavy metals forming anomalies in the study area were Pb, Zn, Cu, As and Cr with maximum concentrations of 57, 157, 313, 73 and 888 mg/g, respectively. The concentrations of the metals along the streams were high near the anomalies, but decreased downstream.

The anomalies were located over the pegmatite and granite bodies that formed the topographic highs in the area. The occurrence of heavy metal anomalies over the identified pegmatite and granite domes suggests that these rocks were the source of heavy metals and that the anomalous values were due to weathering and residual accumulation with maximum values at the top of the dome.

A comparison of the average concentrations of Pb, Zn, Cu and Cr, pH and electrical conductivity values with water quality guidelines (DWAF, 996; WHO, 2003; and EPA, 2009)

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revealed that these parameters meet the water quality requirements at Ebenezer Dam for domestic, agricultural, livestock and aquatic ecosystem uses.

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